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CALCULATION-GRAPHIC ANALYSIS OF THE IR SPECTRUM OF A GLASS BATCH CONTAINING SODIUM BORATE AND SILICATE AND BORIC AND SILICIC ACIDS

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A calculation-graphic analysis of the IR spectra of sodium borate and silicate as components of a glass batch, obtained in aqueous medium, and probable contaminants — boric and silicic acids — was conducted. It was found that several bands called critical coincide or are close together in the spectrum. Among them are the bands at 947–959, 1004–1005, 1079–1086, 1195–1200, 1450–1453, and 1686–1690 cm^{-1} characterizing the fundamental vibrations of the atoms in bonds in cross-linking groups, and they cannot be distinguished by either the wavenumber or the intensity so that it is impossible to identify the phases formed. The concept of “conditionally distinguishable bands” in the spectra of comparable substances was introduced. The absolute degrees of difference in the wavenumber and intensity, order of sorting the bands, and determination of the boundaries of the critical regions of the spectrum of the batch were examined.

The alkali borosilicate system is used as the basic glass-forming system both in industry and in research, but determining its phase composition, for borosilicates in particular, is somewhat complicated. IR spectroscopy is an effective method of investigating the structure and phase composition of substances. Nevertheless, a total of two bands — at 640 and 920 cm^{-1} — is indicated in [1], for example, for the Si–O–B bond in the spectrum of $5\text{ZnO} \cdot 15\text{B}_2\text{O}_3 \cdot 80\text{SiO}_2$ without specifying the type of vibrations. These data are clearly insufficient for conducting an analysis. In contrast to borosilicates, borates and silicates have been much better investigated individually. Of the many publications, we cite three domestic popular textbooks [2–4]. The use of modern precision spectrometers significantly expands the capabilities of analytical practice, but in conditions where more detailed information can be obtained than previously, special attention should be focused on a comparative analysis of the IR spectra of the individual components.

For this reason, we investigated a sodium borosilicate system using a NEXUS IR Fourier spectrometer. We report the results for sodium borate and silicate and boric and silicic acids as components of the batch for fabrication of micro-

spheres — gas microcontainers [5]. The wavenumber ν and intensity I of the bands in the IR spectra of these components are reported in Table 1.

Acids were used to synthesize the sodium silicate and borate — special-purity (SP) silicic and analytically pure (AP) orthoboric (henceforth “boric”) acids, AP sodium hydroxide, distilled water, and LACHEMA universal indicator. Solutions of sodium hydroxide, boric acid, and an aqueous suspension of silicic acid were prepared first. The alkali solution was added to the suspension before it had completely dissolved, monitored visually, while continuously stirring and heating in a MM-5 magnetic stirrer. The boric acid solution was added to the sodium hydroxide solution (dark blue indicator color) with a P-1 pipette dispenser while stirring without heating to neutral reaction of the medium (indicator colorless). The silicate and borate solutions were individually air-dried in polymer trays by natural evaporation of water. A borosilicate solution was prepared by again stirring the synthesized borate and silicate solutions and then again air-dried. The entire synthesis procedure was repeated ten times.

After drying, 0.01 g of each substance was sampled on a Sartogism balance with an accuracy of ± 0.02 mg and 0.3 g of potassium bromide was added. The mixtures were ground for 1 min in a vibrator (grinding bodies — steel ShKh15

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TABLE 1

Sodium borate, v, cm ⁻¹ /I, %	Sodium silicate, v, cm ⁻¹ /I, %	Boric acid, v, cm ⁻¹ /I, %	Silicic acid, v, cm ⁻¹ /I, %
462/59	1393/81	458/100	409/3
469/59	1414/82	566/71	418/7
503/60	1428/83	785/76	462/1
531/67	1448/86	868/81	548/80
579/91	1459/93	959/91	599/35
605/97	1545/95	1004/99	650/75
653/87	1559/56	1037/100	676/66
677/77	1572/52	1130/89	746/82
726/60	1634/49	1363/49	815/93
772/73	1641/50	1392/51	883/61
800/78	1650/54	1421/20	938/28
830/89	1662/58	1453/61	1015/21
849/100	1690/61	1477/63	1062/21
883/75	1700/73	1580/51	1119/56
947/86	1717/73	1686/57	1195/96
1005/92	1731/70	1714/20	1230/75
1021/89	2110/67	1767/55	1285/88
1062/82	2271/28	2371/49	
1079/85	2379/30	3294/55	
1097/84	2442/30	3469/37	
1131/80	2498/35	3613/47	
1162/86	2605/33		
1217/85	2952/34		
1253/85	3048/56		
1269/83	3339/56		
1343/88	3467/50		
1386/81	3500/54		

beads) then individually placed in a sample holder and then in the diffuse reflection module of the NEXUS IR Fourier spectrometer. The spectra were recorded in the 4000 – 400 cm⁻¹ region with resolution of 4 – 8 cm⁻¹ (Fig. 1).²

An x-ray analysis of the substances was also conducted with DRON-3M and RIGAKU Dmax/RC diffractometers. The phases were identified in the automatic mode with a computer card file: the elements contained in the investigated substances, Na, Si, B, C, O, H were entered first, then the accuracy of agreement of the real and standard data was assessed and the phase composition of the substances was definitively established. The x-ray of the borosilicate exhibited differences from the x-ray for sodium silicate and borate, which indicated the probability of synthesis of borosilicates, but there are no cards for borosilicates in the International Center for Diffraction Data data base (1989). Na₂SiO₃, 160,839;

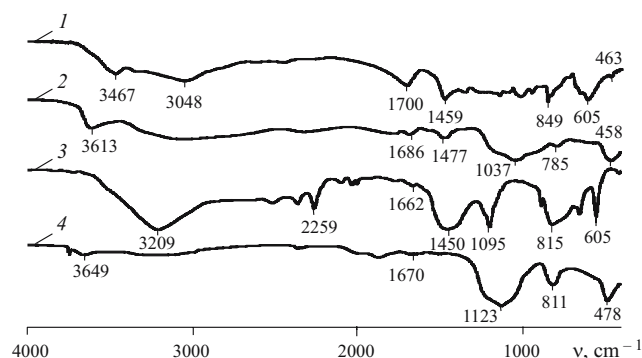


Fig. 1. IR spectra of the components of batch: 1 and 2) sodium borate and silicate, respectively; 3 and 4) boric and silicic acids, respectively.

Na₂Si₂O₅, 181,242; NaBO₂ · 2H₂O, 60,122; Na₂B₂O₄ · 8H₂O, 90,011; and HBO₂ (150,403) were determined (the card numbers are indicated). The comparative analysis revealed a number of distinctive features and signs of similarity of the x-rays of both substances. We found that three silicate and borate reflections coincided, but 19 reflections remained unidentified (Table 2), i.e., the x-ray analysis did not produce complete information on the products of synthesis.

The SiO₂ : H₂O mass ratio in the “silicic acid” reagent was determined with the methods in [6, 7]³ and was 80 : 20 (theoretically, 77 : 23, and the weight loss on calcination was within the limits of 20 – 28%), i.e., SiO₂ : H₂O ≡ H₂SiO₃.

The IR spectra of sodium silicate and borate consisted of bands with blurred (diffuse) and narrow sharp peaks, respectively, and this indicated the amorphicity of the structure of the silicate and the more crystalline structure of the borate. At the same time, some bands in the spectra of sodium borate and silicate coincided or were positioned relatively close together; we call them critical, which necessitated conducting a comparative analysis of the spectra of these and the initial substances, since acids or the products of their decomposition could be present as contaminants in the synthesized batches. Determination of the distinguishability of the bands of a critical group in the spectra of sodium borate NaB and silicate NaSi, and boric HB and silicic HSi acids is reported in Table 3.

The absolute degree of different Δ in parameters v and I was calculated with the bands of the critical group with the general equation:

$$\Delta = \left| 100 - \frac{100p_{\min}}{p_{\max}} \right|,$$

where p_{\min} and p_{\max} are the smallest and largest parameters of the compared bands.

² The IR spectroscopic data were provided by our colleague at the Russian Federal Nuclear Center – All-Russia Research Institute of Experimental Physics (RFNC – ARIEP), A. Sh. Komarevskaya.

³ The analysis was performed with the method in [6] by colleagues at RFNC – ARIEP E. G. Orlikova and I. V. Astakhova and by E. F. Medvedev with the method in [7].

The bands were considered indistinguishable and consequently unsuitable for determination of the substances when they were simultaneously present in the batch if $\Delta \leq 10\%$ for both parameters (ν and I). If $\Delta > 10\%$ for one of them, the bands were considered conditionally usable. The bands could be used for IR analysis of substances without reservations when $\Delta > 10\%$ for both parameters. All bands except for the critical bands were assigned to the last type in the present study (see Table 1). We cite two examples from Table 3 to illustrate the practical application of the equation for determination of Δ .

Example 1. Consider a pair of bands from the spectra of sodium borate and silicic acid: $\nu_{\text{NaB}} = 531 \text{ cm}^{-1}$, $I_{\text{NaB}} = 61\%$; $\nu_{\text{HSi}} = 524 \text{ cm}^{-1}$, $I_{\text{HSi}} = 61\%$:

$$\Delta_{\nu} = \left| 100 - \frac{100 \times 524}{531} \right| = 1.3\% < 10\%;$$

the bands are indistinguishable based on parameter ν ;

$$\Delta I = 0;$$

the bands are also indistinguishable based on parameter I .

Conclusion: The bands of sodium borate and silicic acid are indistinguishable in the overall IR spectrum and cannot be used for identifying the substances.

Example 2. Consider a pair of bands from the spectra of sodium borate and silicate: $\nu_{\text{NaB}} = 1393 \text{ cm}^{-1}$, $I_{\text{NaB}} = 81\%$; $\nu_{\text{NaSi}} = 1392 \text{ cm}^{-1}$, $I_{\text{NaSi}} = 51\%$:

$$\Delta_{\nu} = \left| 100 - \frac{100 \times 1392}{1393} \right| = 0.1\% < 10\%;$$

the bands are cannot be distinguished with respect to the position in the spectrum;

$$\Delta_I = \left| 100 - \frac{100 \times 51}{81} \right| = 37\% > 10\%;$$

the bands can be distinguished by the intensity.

Conclusion: the bands cannot be distinguished based on the position in the overall IR spectrum but can be distinguished with respect to the intensity, and they can conditionally be used for identification of sodium borate and silicate.

The overall IR spectrum contained 30 indistinguishable or conditionally distinguishable bands for sodium borate and 14 for sodium silicate; acids and their derivatives: 24 for boric, 15 for silicic (see Table 3). The reason for this is most probably the closeness of the structures of these substances. In synthesizing the solutions, the ratio of the concentrations of silicon and sodium oxides (silicate ratio) was maintained at three, which indicated formation of a laminar two-dimensional silicate network [8, 9]. The $[\text{SiO}_4]$ tetrahedron is the basic structure of silicates and silicic acid. Boroxol rings of $[\text{BO}_3]$ triangles form the boric acid network, but the boron atom is actually located some distance from the plane con-

TABLE 2

Angle of reflection 2Θ , deg	Intensity I , 10^{-3} CPS, * sec - 1	Comments
31.1	91.0	Coincidence of reflections of NaBO_2 and $\text{Na}_2\text{Si}_2\text{O}_5$
34.3	100.0	
37.0	38.6	
18.1	20.4	In the region of angles $2\Theta = 18 - 71^\circ$, the reflections were not identified; the most intense reflections in this region are separated by the dashed line
22.2	20.4	
25.4	13.6	
51.5	13.6	
52.6	20.5	
55.2	13.6	
56.1	6.8	
57.8	11.4	
59.4	2.3	
61.1	2.3	
60.9	4.5	
62.0	2.3	
65.0	4.5	
66.5	2.3	
67.0	6.8	
68.1	2.3	
68.7	2.3	
69.8	2.3	
70.7	4.5	

* CPS: counts per second.

taining the oxygen atoms [10], forming a pseudotetrahedron. Each oxygen atom in sodium oxide positioned between two $[\text{BO}_3]$ pseudotetrahedrons causes the formation of two complete $[\text{BO}_4]$ tetrahedrons joined through the apices. A two-dimensional planar structure is also characteristic of sodium borate, like boric acid. The similarity of the structures causes formation of a combined borosilicate network and could be the cause of the great similarity of the IR spectra of these salts and acids.

In comparing the spectra of the substances by pairs (see Table 3 and Fig. 2), it was found that none of them can be used for identification of the substances if the position of the critical bands in the spectrum alone (ν) is considered, since the 10% barrier was not surmounted in any case with respect to the absolute degree of difference Δ_{ν} . However, with respect to the intensity, some of the bands of this group can be used for analyzing the IR spectra, although some bands also entered the 10% region of indistinguishability for all pairs of substances except for the boric acid/sodium silicate pair (see Fig. 2b).

The first derivatives $\partial\Delta/\partial p$ were found to more precisely define the boundaries of the critical regions of the IR spectra. The first derivative of a function (in the given case, the absolute degrees of difference Δ_{ν} and Δ_I for the wavenumber) is

TABLE 3

Fragment of the spectrum, ν , cm^{-1}/I , %					Absolute degree of difference, Δ_ν/Δ_I , %					Distinguishability of the bands	
NaB	HB	NaSi	HSi	HB – HSi	NaB – HB	NaB – NaSi	NaB – HSi	NaSi – HSi	HB – NaSi	ν	I
	418/7		420/70	0.5/90						–	+
462/59	462/1	458/100			0/98.3	0.9/41			0.9/99	–*	+*
469/59	462/1				1.5/98.3					–	+
531/61			524/61				1.3/0			–	+
	548/80		550/56	0.4/30						–	+
		566/71	566/53					0/25.3		–	+
605/97	599/35				1/63.9					–	+
653/87	650/75				0.5/13.8					–	+
677/77	676/66				0.1/14.3					–	+
883/75	883/61				0/18.7					–	+
947/86	938/28				0.9/67.4					–	–
947/86		959/91				1.3/5.5				–	–
1005/92		1004/99				0.1/7.1				–	+
1021/89	1015/21				0.6/76.4					–	+
		1037/100	1034/82					0.3/18		–	+
1062/82	1062/21				0/74.4					–	–
1079/85			1086/95				0.6/10.5			–	+
1097/84			1086/95				1/11.6			–	+
	1119/56		1123/100	0.4/44						–	–
	1195/96		1200/88	0.4/8.3						–	+
1269/83			1264/61				0.4/26.5			–	+
	1285/88		1293/30	0.6/65.9						–	+
1343/88			1350/23				0.5/73.9			–	+
1393/81		1392/51				0.1/37				–	+
1414/82		1421/20				0.5/75.6				–	+
1428/83		1421/20				0.5/75.9				–	+
1448/86	1450/100	1453/61			0.1/17	0.3/29.1			0.2/39	–	+
1459/93	1450/100	1453/61		0.2/39	0.6/7	0.4/34.4				–	–
1572/52		1580/51				0.2/6.6				–	+
1662/58	1662/28				0/51.7					–	–
1690/61		1686/57				0.2/6.6				–	+
1717/73		1714/20				0.2/72.6				–**	+**
	1763/18	1767/55							0.2/67.3	–***	+***
	1927/15		1937/14	0.5/6.7						–	+
	1998/23		1992/14	0.3/39.1						–	+
2110/67	2095/22				0.7/67.2					–	+
	2259/66		2264/3	0.2/95.4						–	+
2271/28			2264/3				0.3/89.3			–	+
2379/30		2371/49				0.3/38.8				–	+
2952/34	2950/62				0.1/45.2					–	+
	3209/100		3198/17	0.3/83						–	+
3467/50		3469/37				0.1/26				–	+
3500/54	3500/34				0/37					–	+

Note. Compared pairs of bands * NaB – HB, HB – NaSi, (NaB – HB) – (NaB – HSi); ** NaB – HB, HB – NaSi, (NaB – HB) – (NaB – HSi); *** NaB – HB, HB – NaSi, (HB – HSi) – (NaB – HB), (NaB – HB) – (NaB – HSi) are indistinguishable by wavenumbers ν (–) but are distinguishable by intensities I (+).

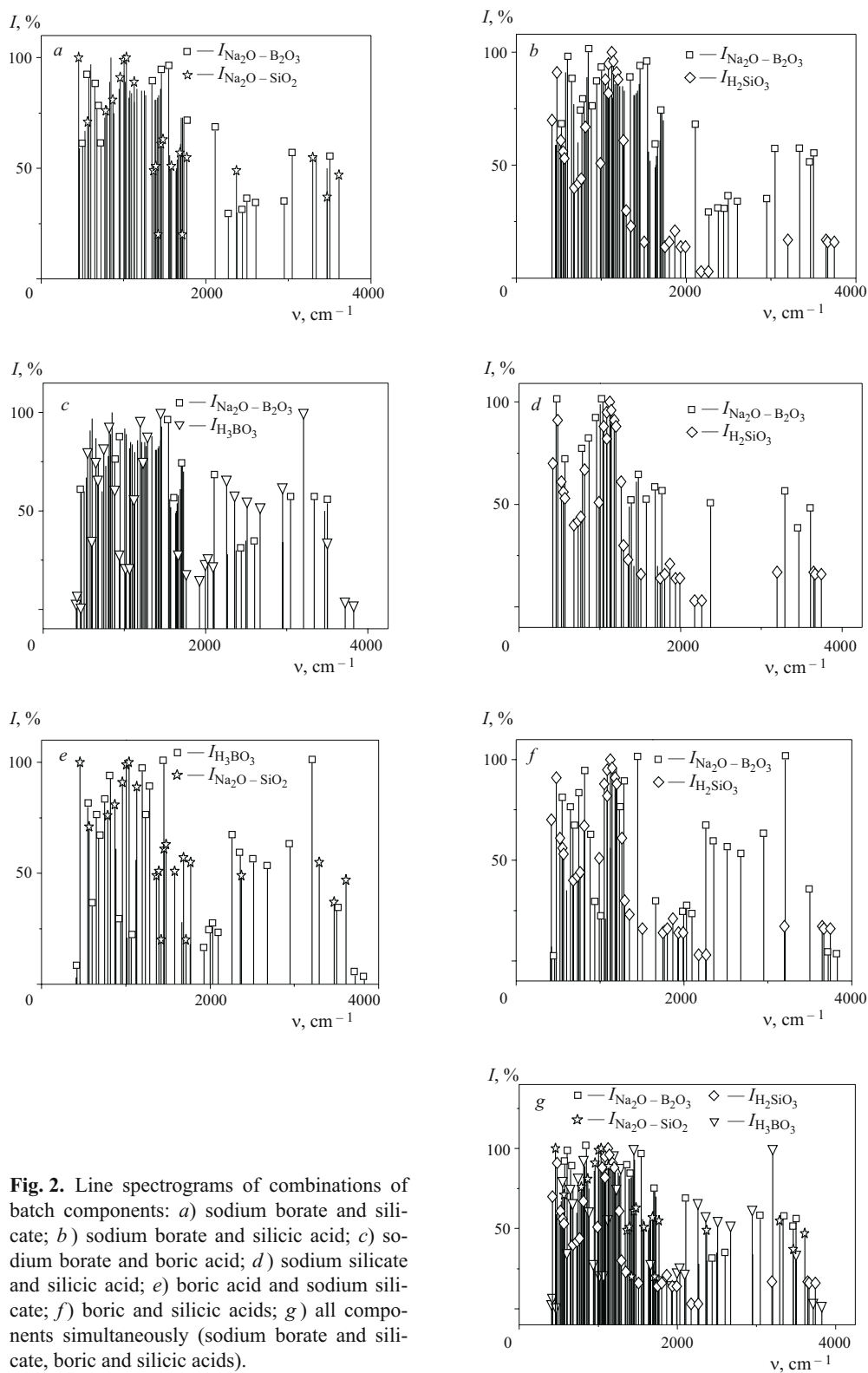


Fig. 2. Line spectrograms of combinations of batch components: *a*) sodium borate and silicate; *b*) sodium borate and silicic acid; *c*) sodium borate and boric acid; *d*) sodium silicate and silicic acid; *e*) boric acid and sodium silicate; *f*) boric and silicic acids; *g*) all components simultaneously (sodium borate and silicate, boric and silicic acids).

simply the rate of the change. The sign of the derivative is of no importance. In principle, the process can be accelerated or inhibited, i.e., the rate can be negative or positive. However, for determining the boundaries of the change, the sign is not as important as the fact that a process which is materially

manifested by a change in or constancy of some property, parameter, etc., takes place. Constancy corresponds to zero rates and numerical values are obtained differently. With respect to the examined IR spectra, nonzero values are equivalent to inhibition — making data analysis difficult, while

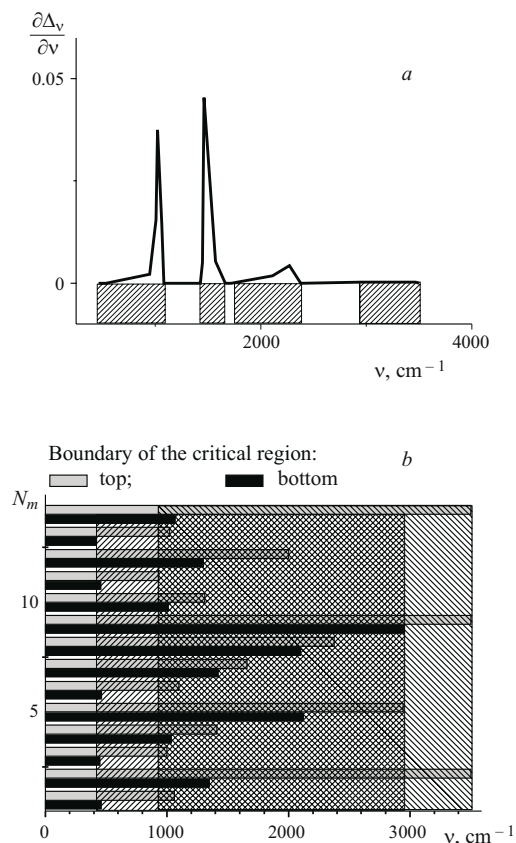


Fig. 3. Distribution of the first derivative of the absolute degree of difference Δ_v with respect to the position of the bands of the critical group in the IR spectrum and the critical regions of the spectrum of a four-component mixture: *a*) first derivative $\partial\Delta_v/\partial\nu$ for a two-component mixture; *b*) critical regions of the spectrum of the four-component mixture.

zero values defined the regions where the bands of the compounds were located based on the wavenumber and intensity different from the bands of the other components of the batch — definite bands. The values of Δ_v and Δ_I *a priori* exceeded the 10% barrier for them, so that they were removed from the mass of critical values and replaced by zeros. As a consequence, the mass of nonzero values in the mass of zero values was the critical region.

We will explain the above with the following example. The data for sodium borate and boric acid were taken from Table 3. The first derivative $\partial\Delta_v/\partial\nu$ was determined first. The partial derivatives from division of the differences between two neighboring values of Δ_v and the corresponding wavenumbers ν were calculated, i.e., the sorting step for data on Δ_v and ν was

$$(i + 1) - i = 1,$$

where i is the preceding value; $(i + 1)$ is the next value up to $i = \max$ (entire mass of data).

A graphic dependence was plotted with the values obtained (Fig. 3a). The perpendiculars from the initial and final

points of the peaks were then applied on the abscissa and the boundaries of the regions of the critical bands were determined under them (separated by hatching): 460 – 1076 cm^{-1} — first critical band region, 1424 – 1665 cm^{-1} — second region, 1750 – 2380 cm^{-1} — third, and 2935 – 3500 cm^{-1} — fourth region. It is not difficult to see that the boundaries determined by calculation totally agree with the data in Table 3.

The boundaries of the critical regions with respect to parameter ν for all combinations of components were determined similarly (see Table 3) and the results are reported below.

Batch components	Boundaries of critical region, cm^{-1}
Sodium borate – sodium silicate . . .	460 – 1061, 1347 – 3500
Sodium borate – silicic acid . . .	450 – 1000, 1035 – 1411, 2122 – 2944
Sodium borate – boric acid . . .	462 – 1100, 1420 – 1660, 2100 – 2375, 2952 – 3500
Sodium silicate – silicic acid	1011 – 1311
Boric acid – sodium silicate	456 – 933, 1300 – 2000
Boric acid – silicic acid	420 – 1022, 1067 – 3500

For all substances except for the sodium silicate – silicic acid pair, almost the entire region of the IR spectrum, from short- to long-wave, is critical. This indicates not only the great similarity of the structures of the compared substances, but also the presence of contaminants of the initial substances (boric and silicic acids) in the target products of synthesis — sodium borate and silicate. With respect to the separated pair, we can say that since the number of critical bands is minimal, sodium silicate was more completely synthesized and the silicic acid contaminant was insignificant. The fundamental vibrations of the O – Si – O bond in the structure of the high- and low-silica sodium silicates are located in the 1011 – 1311 cm^{-1} region [11, 12].

On the whole, 14 critical regions ($N_m = 14$) were determined, and their boundaries are shown in the diagram in Fig. 3b. The regions of minimum (420 – 2952 cm^{-1}) and maximum (933 – 3500 cm^{-1}) values of ν in the paired comparison of the spectra of the substances are separated by the hatching. The region of intersection of the hatched parts defined the region of the critical bands in the spectrum at 933 – 2952 cm^{-1} when all substances were present in the batch simultaneously. The fundamental bands of sodium borate and silicate and boric and silicic acids are located in the separated IR region. In their determination in the batch, this region of the spectrum is the most complex. After revealing the critical bands, attention should be turned to their intensity — it is highly probable that the bands that coincide on this parameter can be distinguished and used for identification of the substances, otherwise the critical bands must be excluded from the examination, since determination of the substances in the mixture based on these bands is not possible.

If we use the IR spectra of the components alone (see Fig. 1), their digital files (see Table 1; the spectra are not re-

ported in some publications), the line spectrograms (for example, in Fig. 2g), or the data on the change in the absolute degrees of difference for the wavenumber and intensity, then it is somewhat difficult to accurately determine the boundaries of the critical band region for a mixture of components. On the contrary, the method presented here allows doing this, and complicated mathematical calculations are not required.

The calculation-graphic method of processing IR spectra for subsequent identification of substances in a mixture (batch) thus consists of the following:

taking the IR spectra of a multicomponent batch, its ingredients, and initial reagents (in the case of a synthetic batch);

accurately determining the wavenumbers and intensities of the bands;

calculating the absolute degrees of difference for the wavenumbers Δ_v and intensities Δ_I ;

sorting the bands: if $\Delta_v < 10\%$ and $\Delta_I < 10\%$ at the same time, the bands cannot be used for identifying the substances; if $\Delta > 10\%$ for one of the parameters, the bands can conditionally be used for the analysis; if $\Delta > 10\%$ for both parameters, the bands can be used for determining the substances in the batch;

calculating the first derivatives $\partial\Delta_v/\partial v$, $\partial\Delta_I/\partial v$ and determining the boundaries of the spectral regions of the critical bands;

identifying the batch components with the bands remaining after sorting.

We found with the calculation-graphic method that there are 40 conditionally distinguishable and 9 indistinguishable bands in the IR spectrum of a batch as a mixture of four components, and of these, the bands with maxima at 947–959, 1004–1005, 1079–1086, 1195–1200, 1450–15453, and 1686–1690 cm^{-1} characterize the fundamental vibrations of the atoms in the bonds in cross-linking groups. This can cause the similarity of the structures of sodium borate and silicate and boric and silicic acids.

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